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Final Research Report

January 30, 1963

A Study of the Properties of Matter
by Means of Nuclear Magnetic Resonance

H. C. Torrey and H. Y. Carr, Principal Investigators
Department of Physics, Rutgers - The State University
New Brunswick, New Jersey

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Semitechnical Brief

This report summarizes the work which was done under Contract AF49-
(638)-755 during the period January 1, 1960 to December 31, 1962.

The small magnets contained in the nuclei of the materials studied provide a means to investigate microscopic details of the environment surrounding the nuclei. These very small magnets transmit signals at a resonance frequency determined in the first approximation by the values of a strong externally applied magnetic field. But the detailed shapes, intensities, and time dependence of the transmitted signals are determined by the electric and magnetic fields associated with the local nuclear environment. By interpreting detailed properties we have gained valuable information concerning the coupling in electron-nuclear systems, the local magnetic fields present during molecular collisions in simple monatomic fluids such as xenon, and the fundamental interactions present in the important diatomic fluid, hydrogen.

This work is described in detail in scientific papers published in connection with this contract. They are listed as references in this report.

I. Introduction

The work under this contract is summarized in Section II of this report under three general projects:

1. Double Resonance Experiments on Dipolar Coupled Electron-Nuclear Systems.
2. Nuclear Magnetic Resonance Studies of the Liquid and Gaseous States of Ixonatomic Systems.
3. Nuclear Magnetic Resonance Studies of Liquid and Gaseous Hydrogen.

Detailed descriptions of this work are given in the references listed in the summaries. Except for the abstracts of talks given at meeting of the American Physical Society, all of the scientific papers related to this work which have been published or submitted for publication have simultaneously been submitted to the Air Force Office of Scientific Research as technical reports. A bibliography of the scientific papers is given in Section III.

Section IV of the report contains general information concerning personnel, financial support, and other administrative items.

II. Summary of Scientific Work

1. Double Resonance Experiments on Dipolar Coupled Electron-Nuclear Systems

We have made extensive observations of relaxation of proton spins coupled by static dipolar-interactions to electron spins. The measurements were made as a function of the microwave power at frequencies in the neighborhood of the electron spin resonance. Not only was this resonance excited but also double flip transitions of the coupled electron-proton systems.

The materials studied were: (1) asphalt, (2) 5% Ce in $(Ce,La)_2Fe_3(NO_3)_{12} \cdot 24H_2O$, abbreviated GMN, (3) and (4) 1% and 10% by weight of diphenyl picryl hydrazil (DPPH) dissolved in polystyrene, and (5) a solid organic free radical salt: tris p-aminophenyl aminium perchlorate, (AMI).

The first four of these samples display the type of enhancement of proton polarization caused by double-flip transitions, the fifth shows this type of enhancement at low temperatures (1.7°K) but at room temperature only the Overhauser type of enhancement produced by saturating the electron spin resonance.

In all cases (except for AMI at room temperature) we have found the following typical behavior of the proton relaxation times, T_{1N} , as a function of the microwave power and frequency.

The "normal" T_{1N} is found when the microwave power is decreased to zero after it had been on long enough to produce an enhancement of the proton polarization. That is the protons relaxed from an enhanced polarization to the thermal equilibrium polarization with the normal T_{1N} .

When the microwave power was turned on after the proton spins had reached thermal equilibrium, the proton spin polarization approached the final enhanced steady state value with a value of T_{1N} which was shorter than the "normal" T_{1N} if the polarization was produced by double spin flips provided the microwave frequency was far enough off the electron spin resonance center frequency so that the electron spins were not saturated. If, however, the microwave frequency was sufficiently close to the center of the electron spin resonance so as to saturate the electron spins, the observed proton relaxation time to the enhanced state was longer than the normal time, in some cases by more than an order of magnitude. The latter effect is anomalous. At least we have not been able to find a satisfactory

explanation for it.

We present a summary of the results in the accompanying table.

Sample	T_{LN}^0 (sec)	$T_{LN}^{(+)}$ (sec)	$T_{LN}^{(e)}$ (sec)
Asphalt	4.0	1.15	6.75
10% DPMI	0.026	0.010	2.25
1% DPMI 77°K	0.036	0.014	1.84
	0.087	0.045	1.35
AlII	0.116	0.045	*
CLN	1.28	0.145	4.80

*Not possible to measure.

Table I Measured nuclear relaxation times. T_{LN}^0 is the thermal equilibrium relaxation rate. $T_{LN}^{(e)}$ was measured in the presence of electron resonance excitation and $T_{LN}^{(+)}$ when double flip transitions were induced. The determination of $T_{LN}^{(+)}$ was made with the external field set to give maximum positive enhancement, not at the center of the double-flip absorption line.

Here, T_{LN}^0 is the "normal" relaxation time; $T_{LN}^{(+)}$ is the relaxation time for relaxation to the enhanced state when the electron spins are not saturated; $T_{LN}^{(e)}$ is the same with the electron spins saturated. The

fact that $T_{1N}^{(+)} < T_{1N}^0$ is to be expected because of the extra path for relaxation provided by the double spin flips. What is so unexpected is the extraordinarily long value of $T_{1N}^{(e)}$ in the last column. We have tried to explain this effect by a change in the effective correlation time τ_c' for the dipolar field from the value τ_c^0 to a shorter value produced by forced electron spin flips

$$\frac{1}{\tau_c'} = \frac{1}{\tau_c^0} + \gamma_e^2 H_{ce}^2 T_{2e}$$

This equation can be derived from the transient solutions of the Bloch equations (H. C. Torrey, Phys. Rev. 76, 1059 (1949)). Unfortunately it is found that a longer τ_c' rather than a shorter is required to explain the results for $T_{1N}^{(e)}$.

We are still searching for an adequate explanation of this effect and will refrain from publishing our results (aside from the abstract Bull. Am. Phys. Soc. II 7, 85 (1962)) until more light can be thrown on this matter.

2. Nuclear Magnetic Resonance Studies of the Liquid and Gaseous States of Monatomic Systems

A year or two prior to the beginning of this contract, R. L. Streever and H. Y. Carr (working under our previous Air Force contract) initiated a study of gaseous and liquid xenon using NMR techniques. Previous studies of xenon had emphasized the measurement of magnetic moments; but some evidence had been gathered to indicate that at least in the case of the isotope Xe^{129} the spin-lattice relaxation rate was 4 or 5 orders of magnitude more rapid than could be expected from the obvious direct nuclear dipole interaction. We were interested in this problem not only in order to investigate the large discrepancy, but more especially because we

believed the simple Xe^{129} (monatomic and spin $\frac{1}{2}$) system might provide the simplest and best possible example of a classical fluid for NMR studies.

Streever and Carr prepared purer samples than were previously available. By so doing they reduced the relaxation rate discrepancy to 2 to 3 order magnitudes. But the rate still could not be accounted for by the dipole-dipole mechanism. However, in their work they discovered a strong shift in the xenon resonance which varies linearly with the fluid density over a very large range (0 to 500 amagats). As the density increases, the shift in the local field at the nucleus increases in the direction of the externally applied field. It can be described as a decrease in the normal diamagnetic correction appropriate to an isolated atom, or alternatively as a separate paramagnetic correction. For dense samples (the order of a few hundred amagats) in a field the order of 10^4 gauss, the shift is the order of 1 gauss. The normal diamagnetic shift in this case is approximately 50 gauss. The early work by Streever and Carr is described in a scientific paper completed during the first year of the contract now being summarized. The paper was published in the Phys. Rev. 121, 20 (1961) and submitted to the Air Force as a technical note.

The experimental work has been continued under this contract. The field dependence of the shift was established and the previously observed density dependence confirmed:

$$\Delta H = + (4.22 \pm .05) \times 10^{-7} \rho H_0,$$

where the fields are in gauss and the density ρ in amagats. The shift in the Xe^{131} resonance was checked in some exploratory measurements and found to be identical to that in the Xe^{129} resonance. The density dependence of the Xe^{129} spin-lattice relaxation rate was more accurately

studied and found to be:

$$\frac{1}{T_1} = (5.0 \pm .5) \times 10^{-6} \rho,$$

where the relaxation time T_1 is in sec and the density again in amagats. (This order of magnitude for the rate, however, still cannot be accounted for by the direct dipole interaction.) An unusual density independent behavior was found for the Xe^{129} relaxation rate in the liquid in equilibrium with its vapor pressure. Finally the self-diffusion coefficient was measured at various points in both the gas and liquid. The experimental work has been described in detail in a scientific paper by E. R. Hunt and H. Y. Carr submitted for publication to the Physical Review. The paper has also been submitted to the Air Force as a technical note.

H. C. Torrey has made a theoretical study to determine if the fluctuating magnetic fields due to the rotation of a diatomic charge configuration during collisions might account for the Xe^{129} relaxation rate and shift. Using Ramsey's theory of chemical shifts in linear molecules (e.g., hydrogen), Torrey has been able to calibrate the spin-rotational coupling in terms of the observed density-proportional chemical shift. The value of the coupling is found to be of the correct magnitude to account for the observed relaxation of Xe^{129} in xenon gas. Although this does not represent an independent theoretical calculation of the relaxation from first principles, it does represent the first successful explanation of the relationships between the various Xe^{129} data. This work is described in detail in a scientific paper prepared by Torrey for publication. It also has been submitted to the Air Force as a technical note.

3. Nuclear Magnetic Resonance Studies of Liquid and Gaseous Hydrogen

Our work in this area was initiated by L. Lipsicas, research associate, as a continuation of previous work done by himself and M. Bloom at the University of British Columbia. This previous work is described in the Canadian Journal of Physics 39, 881 (1961). The experimental work done at Rutgers under this contract involves measurements of the self-diffusion coefficient and the spin-lattice and spin-spin relaxation times.

(a) Self-Diffusion

The self-diffusion in normal hydrogen gas was studied using NMR free precession techniques. An absolute measurement of D_{11} was made at 78°K and 117 amagats. Relative measurements of D_{11} as a function of gas density were made at 55°, 78°, and 90°K using gas densities up to 650 amagats. The observed density dependence of D_{11} was found to be in marked disagreement with the Enskog dense-gas theory. A detailed description of this work and a discussion of the results was published in the Journal of Chemical Physics 36, 1235 (1962). This paper was submitted to the Air Force as a technical note.

More recently the self-diffusion in a mixture of 37.5% orthohydrogen--62.5% parahydrogen at 20.35°K has been measured. The results indicate that ortho-molecules in different spin quantum states must be treated as distinguishable particles in calculating the diffusion cross-sections. This is in contradiction to the earlier assumption of indistinguishability by Cohen, et.al. (Physica 22, 791 (1956)). The experimental results have been reported and discussed in Physics Letters 3, 212 (1963). Reprints of this work will be distributed as an Air Force technical note when available. The temperature dependence of the diffusion over the range 20°K to 90°K has also been investigated and found to be in reasonable

agreement with theory when allowance is made for the above symmetry effects.

(b) Spin Relaxation

The improved magnet homogeneity available in the present work was used to check the earlier report by Lipsicas and Bloom that the spin-spin time T_2 and the spin-lattice relaxation time T_1 in hydrogen gas were not equal. A more accurate and reliable measurement of T_2 at 77.5°K on a gas sample of approximately 100 amagats density indicated that to within the error of $\pm 4\%$, T_1 and T_2 are equal. This result was reported in the Canadian Journal of Physics 40, 382 (1962).

The spin-lattice relaxation time T_1 has been measured as a function of orthohydrogen concentration and density in ortho-parahydrogen gas mixtures over the temperature range 20-400°K. The measurement of T_1 in the dilute gas ($P \leq 400$ amagats) at temperatures above 100°K show a very marked difference between the ranges of the ortho-ortho and ortho-para interactions. Preliminary calculations show that the measured values of T_1 fit an approximately $1/r^6$ range for the ortho-ortho interaction, while the ortho-para interaction is approximately $1/r^{13}$. It is hoped, eventually, to deduce from our T_1 measurements the form of the anisotropic intermolecular potential and the absolute value of the interaction energy. Quantum mechanical diffraction effects have been observed, which at high temperatures increase the mutual separation of the molecules. In the dense gas, $P > 400$ amagats, T_1 increases very rapidly with density, the rate of increase rising very sharply with decreasing temperature. The behavior of T_1 in liquid hydrogen under pressure confirms the intuitive idea that the correlation of the molecules in a liquid is that of a dense gas at low temperatures. This work is still in progress but we anticipate it will be described in detail in a scientific paper by A. Hartland and H. Lipsicas. Such a paper will be submitted to the Air Force as a technical note.

III. Bibliography

Scientific Publications and Papers Read in Connection with Contract AF49(638)-755.

1. "Nuclear Magnetic Resonance of Xe^{129} in Natural Xenon," R. L. Streever and H. Y. Carr, Phys. Rev. 121, 20 (1961).
2. "Changes in Nuclear Spin Relaxation by Irradiation of Electron Resonances," G. E. Schacher and H. C. Torrey, Bull. Am. Phys. Soc. II 7, 85 (1962).
3. "NMR Measurements of Self-Diffusion in Normal Hydrogen Gas from 55° to 900K," M. Lipsicas, J. Chem. Phys. 36, 1235 (1962).
4. "Nuclear Magnetic Resonance of Xe^{129} ," E. R. Hunt and H. Y. Carr, Bull. Am. Phys. Soc. II 7, 293 (1962).
5. "Nuclear Spin-Spin Relaxation," M. Lipsicas and A. Hartland, Can. J. Phys. 40, 382 (1962).
6. "Nuclear Magnetic Resonance of Xe^{129} in Natural Xenon," E. R. Hunt and H. Y. Carr, submitted to the Physical Review.
7. "Chemical Shift and Relaxation of Xe^{129} in Xenon Gas," H. C. Torrey, submitted to the Physical Review.
8. "Quantum Symmetry Effects in Hydrogen Gas," A. Hartland and M. Lipsicas, Phys. Letters 3, 212 (1963).

IV. General Information

1. Personnel Associated with Contract AF49(638)-755.

Principal Investigators: H. C. Torrey and H. Y. Carr

Research Associates:

- (a) Dr. Max Lipsicas (2 years) former student of Dr. M. Bloom at the University of British Columbia, now on the staff of Brookhaven National Laboratory.
- (b) Dr. Anthony Hartland (1 month) former student of Dr. J. G. Powles at the University of London, now a member of the Rutgers Physics Department instructional staff.
- (c) Dr. R. L. Streever (1 month) former graduate student at Rutgers and research assistant under Contract AF18(603)-6, now on the staff of the National Bureau of Standards.

Research Assistants:

- (a) Mr. G. E. Schacher, received Ph. D. degree, now on the staff of the Argonne National Laboratory.

Research Assistants cont'd:

- (b) Mr. E. R. Hunt, received Ph. D. degree, now on the staff of the Department of Physics, Duke University.
- (c) Mr. H. Lurie, received M. S. degree, now on the staff of the research laboratory of Gulton Industries, Inc.
- (d) Mr. J. S. Karra, formerly of the staff of the Tata Institute, Bombay, India, currently a graduate student at Rutgers.
- (e) Mr. B. Pass, currently a graduate student at Rutgers.

It is of interest to note that Dr. James H. Simpson, a former graduate student at Rutgers supported by our previous contract, AFL8(603)-6, is the senior scientist on the magnetic resonance project which recently successfully developed, at the General Precision Laboratories, a gyro-compass for potential use in space travel. The Dr. Simpson's GPL team within General Precision's Aerospace Group worked closely with scientists of the Air Force Aeronautical Systems Div., Wright-Patterson AFB.

2. Summary of Fiscal Record for Contract

Total budget Jan. 1, 1960 to Dec. 31, 1962	\$115,349
Amount spent, Oct. 1 to Dec. 31, 1962*	9,272
Cumulative Expenditures, Jan. 1, 1960 to Dec. 31, 1962*	113,621
Unexpended Balance*	\$ 2,291

*Includes adjustment of Indirect Cost from 55.16% to new audited rate of 51.83%

3. The Principal Investigators for this contract wish to express their appreciation to the Air Force Office of Scientific Research for the support provided through this contract as well as preceding Air Force Contracts. We speak not only for ourselves but also for the university, the department, and all personnel associated with these contracts.

4. The work described in this report, was simultaneously supported by the Rutgers Research Council and an equipment grant from the National Science Foundation.

5. Much of the work described in this report will be continued during the coming two years with financial support from the National Science Foundation Grant GP-229.

Henry C. Torrey
Henry C. Torrey

Herman Y. Carr

Herman Y. Carr
Principal Investigators
Contract AF49(638)-755